

# Arylstearic Acids From Oleic Acid. Variables Affecting the Yield and Properties \*

A. J. STIRTON, B. B. SCHAEFFER,<sup>1</sup> ANNA A. STAWITZKE, J. K. WEIL, and WALDO C. AULT,  
Eastern Regional Research Laboratory,<sup>2</sup> Philadelphia 18, Pennsylvania

NUMEROUS references show the past and current interest in the reaction of an aromatic compound with an olefinic carboxylic acid such as oleic acid. The olefinic acid, the aromatic compound, and the condensing agent may be chosen from a variety of possibilities. In the present paper arylstearic acids, many of them new, prepared for the purpose of cooperation with the Naval Research Laboratory in the evaluation of lubricating oil additives are described. Observations regarding the nature of the reaction, with special attention being given to the use of oleic acid and of "iso-oleic" acid relatively free from linoleic acid, are also reported.

The arylstearic acids, which are prepared by the use of condensing agents of the type of aluminum chloride, are usually viscous oils which do not readily crystallize. This is believed due in part to their composition as a mixture of several isomers, the aryl radical being attached at different aliphatic carbon atoms in the fatty acid chain. Condensing agents of this type may cause migration of the double bond in oleic acid (5, 7, 21, 26), and if this occurs in the Friedel and Crafts reaction, formation of several isomeric arylstearic acids may be expected. Moreover, when substituted aromatic compounds are used in the synthesis, several isomers may be formed by attachment of the oleic acid to different points of the aromatic ring.

We have recently found that under certain conditions arylstearic acids which are solid at room temperature may be isolated in crystalline form. Thus far, we have obtained these solid crystalline acids most readily when using aromatic hydrocarbons which serve to restrict the possible number of isomers. Thus, the first solid crystalline arylstearic acid which we have isolated is obtained by the condensation of *p*-xylene with oleic acid. Solid products are also obtained in low yields by the condensation of *p*-chlorotoluene, *o*-xylene, *o*-chlorotoluene, and benzene with oleic acid.

Arylstearic acids prepared from different aromatic compounds differ in physical and chemical properties. The reaction by which they are prepared is a means of obtaining a selected saturated arylaliphatic carboxylic acid, and it was of interest to further explore the possibilities with readily available aromatic hydrocarbons.

## Yield of Arylstearic Acids

Table I presents the yield and some of the analytical and physical data for 26 arylstearic acids. The reaction conditions were similar to those previously described (32, 33). Generally a 5 to 7 molar ratio of the liquid aromatic compound was used, and a 1.1

molar ratio of the metal halide was added in portions to the oleic acid solution. After all the metal halide had been added and had dissolved, the warm reaction mixture was heated to 80°, and then cooled and hydrolyzed in dilute hydrochloric acid. A petroleum ether or a mixture of a petroleum ether and *o*-dichlorobenzene was used as a solvent for reactions with solid (as well as for some liquid) aromatic compounds.

For the most part commercial oleic acid was used, having an average composition of 70% oleic, 15% linoleic, and 15% saturated fatty acids. The arylstearic acids were vacuum distilled at temperatures from about 220° to 280° at 0.4 mm. The yield was based on the oleic acid content.<sup>3</sup>

The yield, which depends on the aromatic compound, was greatest for technical *m*-xylene (92.4%) and the simpler alkylbenzenes. The yield was lower for aromatic chloro compounds, for compounds used in low molar ratios, for compounds which could easily undergo side reactions with aluminum chloride, and for arylstearic acids of higher molecular weight which could not be as readily vacuum distilled.

Aluminum bromide and zirconium chloride in place of aluminum chloride slightly improved the yield of phenylstearic acid (experiments 2 and 4). The yield of dimethoxyphenylstearic acid (experiment 25), and of xenylstearic acid (experiment 33), recorded in Table I, was increased to 40.5% and to 51.3%, respectively, when zirconium chloride was used as a catalyst in place of aluminum chloride.

An oleic acid of 95% purity (35) did not improve the yield, but the products had notably less color (experiments 5, 6, 9, 12, 13, 14, 15, 16, 17, 19, 20, 21, 22, 26, 29, 30, 32, 33). In experiment 14 a practically colorless xylylstearic acid was obtained from a solid isooleic acid.<sup>4</sup> The color of an undistilled xylylstearic acid made from purified oleic acid compared favorably with some distilled arylstearic acids from commercial oleic acid (for example, 20.0Y, 2.5R, Lovibond 1" cell).

## Reactions in the Preparation of Arylstearic Acids

The crude phenylstearic acid obtained after the Friedel and Crafts reaction, hydrolysis, and recovery of excess benzene by atmospheric or steam distillation is a dark-brown viscous oil when made from commercial oleic acid. On vacuum distillation at about 0.3 mm., three principal fractions are obtained: a lower semi-solid fraction, the phenylstearic acid fraction, and the still residue. This is shown in Fig. 1.

The lower fraction exceeds the expected amount of saturated fatty acids in the commercial oleic acid by about one-third. It is possible that the oleic acid undergoes side reactions whereby it is converted into products which appear in part in the forerun and in

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<sup>1</sup> Present address: Mathieson Alkali Works (Inc.), Research and Development Laboratories, Niagara Falls, N. Y.

<sup>2</sup> One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Dept. of Agriculture.

<sup>3</sup> Yields previously reported (32, 33), were based on a 100% content of oleic acid in commercial oleic acid and should be multiplied by a factor of about 1.4.

<sup>4</sup> Obtained from hydrogenated cottonseed oil supplied by the Southern Regional Research Laboratory and found to be 45% *cis* and 55% *trans* by an iodine absorption method (31).

TABLE I. YIELD AND PROPERTIES OF LIQUID ARYLSTEARIC ACIDS.

NO.	AROMATIC COMPOUND	OLEIC ACID	MOLAR RATIO AROMATIC COMPOUND ÷ OLEIC ACID	YIELD %	NEUTRAL EQUIVALENT		n <sub>D</sub> <sup>25</sup>	d <sub>4</sub> <sup>25</sup>	MOLECULAR REFRACTIVITY		% c <sup>d</sup>		% h <sup>d</sup>		COLOR LOVIBOND 1" CELL	
					FOUND	THEO.			FOUND	THEO.	FOUND	THEO.	FOUND	THEO.	YELLOW	RED
1 <sup>a</sup>	BENZENE	RED OIL	5.4	63.3	363.0	360.6	1.4887	—	—	—	—	—	—	—	4.5	0.4
2	BENZENE (Al Br <sub>3</sub> )	RED OIL	6.1	71.2	360.6	360.6	1.4903	—	—	—	—	—	—	—	4.0	0.2
3	BENZENE (Fe Cl <sub>3</sub> )	RED OIL	21.2	65.5	362.3	360.6	1.4862	0.9329	111.0	111.0	—	—	—	—	7.0	0.5
4	BENZENE (Zr Cl <sub>4</sub> )	RED OIL	6.0	76.3	361.8	360.6	1.4894	0.9360	111.3	111.0	—	—	—	—	3.4	0.4
5 <sup>b</sup>	BENZENE	OLIVE OIL	5.0	60.3	355.2	360.6	—	—	—	—	—	—	—	—	—	—
6	BENZENE	SOLID ISOOLEIC	6.0	55.7	356.0	360.6	1.4879	0.9299	112.1	111.0	—	—	—	—	0.3	0.0
7	TOLUENE	RED OIL	5.0	80.0	369.3	374.6	1.4903	0.9301	116.5	115.6	—	—	—	—	5.4	0.6
8	CUMENE	RED OIL	5.7	82.8	398.0	402.6	1.4856	0.9205	125.5	124.8	80.39	80.54	11.48	11.52	4.0	0.2
9	DODECYLBENZENE	HYDROG. TALLOW	5.0	19.2	530.4	528.9	1.4886	—	—	—	81.84	81.75	11.94	12.19	—	—
10	TECH. m-XYLENE	RED OIL	5.0	92.4	391.0	388.6	1.4921	—	—	—	—	—	—	—	2.7	0.3
11 <sup>c</sup>	TECH. m-XYLENE	RED OIL	5.0	79.0	390.0	388.6	1.4963	—	—	—	—	—	—	—	5.4	0.1
12	TECH. m-XYLENE	HYDROG. TALLOW	6.0	83.7	382.5	388.6	1.4916	—	—	—	—	—	—	—	1.1	0.1
13	TECH. m-XYLENE	LIQUID ISOOLEIC	7.0	62.9	384.0	388.6	1.4911	0.9288	121.2	120.2	—	—	—	—	0.7	—
14	TECH. m-XYLENE	SOLID ISOOLEIC	5.5	69.0	390.8	388.6	1.4913	0.9264	121.6	120.2	80.05	80.35	11.32	11.41	<0.1	—
15 <sup>b</sup>	o-XYLENE	OLIVE OIL	5.0	73.3	386.0	388.6	1.4936	0.9336	121.1	120.2	80.54	80.35	11.43	11.41	0.8	0.0
16	m-XYLENE	OLIVE OIL	5.0	83.0	391.0	388.6	1.4912	0.9254	121.7	120.2	—	—	—	—	<0.1	0.0
17 <sup>c</sup>	m-XYLENE	OLIVE OIL	5.0	73.0	391.1	388.6	1.4911	0.9258	121.6	120.2	—	—	—	—	<0.1	0.0
18 <sup>b</sup>	p-XYLENE	RED OIL	5.0	78.3	387.7	388.6	1.4933	—	—	—	—	—	—	—	9.9	1.2
19 <sup>b</sup>	p-XYLENE	HYDROG. TALLOW	5.5	67.5	386.2	388.6	1.4927	0.9307	121.2	120.2	80.33	80.35	11.35	11.41	2.3	0.0
20 <sup>b</sup>	p-XYLENE	OLIVE OIL	5.0	73.6	389.2	388.6	1.4930	0.9308	121.3	120.2	—	—	—	—	6.0	0.4
21 <sup>c</sup>	p-XYLENE	OLIVE OIL	5.0	17.8	367.9	388.6	1.5017	0.9453	121.3	120.2	—	—	—	—	20.0	4.2
22 <sup>b</sup>	p-XYLENE	SOLID ISOOLEIC	7.2	22.0	386.4	388.6	1.4926	0.9305	121.3	120.2	—	—	—	—	1.0	0.0
23	m-DIISOPROPYLBENZENE	RED OIL	5.0	76.2	441.0	444.7	1.4895	0.9247	138.7	138.7	81.14	81.02	12.02	11.79	15.0	1.5
24	TRIETHYLBENZENE	RED OIL	5.0	54.3	432.5	444.7	1.4939	0.9235	140.2	138.7	80.80	81.02	12.03	11.79	23.0	3.6
25	p-DIMETHOXYBENZENE	RED OIL	2.9	28.3	420.2	420.6	1.4958	0.9845	124.8	123.5	73.84	74.24	10.49	10.54	9.8	2.4
26	PHENYL ETHER	HYDROG. TALLOW	6.0	46.6	455.0	452.7	1.5157	0.9897	138.1	136.7	—	—	—	—	1.0	0.2
27	CHLOROBENZENE	RED OIL	5.0	56.8	390.0	395.0	1.4962	0.9871	116.9	115.3	72.98	72.57	9.95	9.95	10.0	1.1
28 <sup>b</sup>	o-CHLOROTOLUENE	RED OIL	6.0	68.4	408.5	409.0	1.4986	0.9890	121.4	120.5	73.11	73.40	10.20	10.10	3.7	0.4
29 <sup>b</sup>	p-CHLOROTOLUENE	HYDROG. TALLOW	5.5	36.9	406.3	409.0	1.4991	0.9901	121.3	120.5	73.25	73.40	10.05	10.10	1.2	0.0
30	p-CHLOROPHENETOLE	HYDROG. TALLOW	4.9	60.0	442.7	439.1	1.4977	1.0126	128.2	126.3	70.97	71.12	9.83	9.87	0.4	0.0
31	INDAN	RED OIL	5.0	65.5	406.9	400.6	1.5018	0.9550	123.9	122.6	80.89	80.94	11.58	11.07	13.0	1.6
32	CYCLOHEXYLBENZENE	HYDROG. TALLOW	3.0	48.0	442.6	441.7	1.4984	—	—	—	81.20	81.58	11.02	11.18	—	—
33	XENENE	HYDROG. TALLOW	2.0	38.2	432.7	436.7	1.5290	0.9766	137.9	135.1	62.65	62.50	10.15	10.16	2.0	0.1
34	AMYLXENENE	RED OIL	3.0	32.3	500.6	506.8	1.5160	0.9544	160.4	158.2	82.33	82.94	10.94	10.74	26.5	9.4
35	DIBENZOFURAN	RED OIL	2.0	17.5	457.3	450.6	1.5369	1.0193	138.1	134.5	79.06	79.10	9.60	9.39	16.0	1.5
36	NAPHTHALENE	RED OIL	6.0	42.7	421.1	410.6	1.5304	0.9766	130.0	126.3	81.83	81.90	10.46	10.31	24.0	4.1
37	α-METHYLNAPHTHALENE	RED OIL	6.0	19.8	433.9	424.6	1.5318	0.9814	134.1	130.9	81.90	82.02	—	—	27.0	4.4
38	AMYLNAPHTHALENE	RED OIL	2.0	29.2	473.7	480.7	1.5231	0.9584	153.3	153.5	82.34	82.44	11.38	10.93	28.0	5.3
39	DIMETHYLNAPHTHALENE	RED OIL	2.0	29.1	439.5	438.7	1.5296	—	—	—	81.64	82.13	10.60	10.57	25.0	6.0
40	β-ETHOXYNAPHTHALENE	RED OIL	2.9	25.7	456.8	454.7	1.5294	0.9905	141.7	137.8	78.96	79.24	10.13	10.20	17.0	1.7
41	α-CHLORONAPHTHALENE	RED OIL	5.1	19.0	446.6	445.1	1.5340	—	—	—	75.40	75.56	9.21	9.29	—	—

a-UNLESS OTHERWISE NOTED, THE CATALYST WAS  $AlCl_3$ .

b-CRYSTALLINE ARYLSTEARIC ACIDS WERE ISOLATED IN SMALL AMOUNT FROM THE USUAL VISCOUS LIQUID.

c-OLEIC ACID WAS ADDED DROPWISE TO A SUSPENSION OF  $AlCl_3$  IN THE AROMATIC COMPOUND.

d-ANALYSIS BY MARY JANE WELSH OF THIS LABORATORY.

part in the still residue along with the more easily polymerizable linoleic acid.

When an oleic acid of about 95% purity was used, the yield of phenylstearic acid (experiment 5) was not improved and the yield of xylylstearic acid was lowered (experiment 12), a relatively larger proportion of the oleic acid apparently being converted to still residue.

#### Effect of the Method of Addition of Reactants

When the reaction was carried out by the gradual addition of oleic acid to a stirred suspension of aluminum chloride in the aromatic compound, the arylstearic acid was usually deeper in color and the yield of xylylstearic acid was much lower (experiments 11.

17, 21). The relative proportions of forerun, xylylstearic acid, and still residue formed in the two different methods of addition of reactants are shown in Table II. The nature of the forerun in experiment 11 has not been determined.

#### Compounds Related to the Arylstearic Acids

Three compounds related to arylstearic acids were prepared by the methods shown in Table III. Methyl phenylenedistearate had been previously described by Buu-Hoi and Cagniant (7).

#### Crystalline Arylstearic Acids

Crystalline arylstearic acids which melt above room temperature have been isolated from the condensation products of oleic acid with p-xylene, o-xylene, p-chlorotoluene, o-chlorotoluene, and benzene. It will be noted that insofar as the possible point of attachment of the oleic acid to the substituted aromatic nucleus is concerned, that in the case of p-xylene and benzene only one possible isomer can result while in the other two cases one seems likely to predominate. Properties of the resulting crystalline acids are shown in Table IV. Harmon and Marvel (12) have prepared synthetic 9- and 10-phenylstearic acids which they reported to melt at 36.5°-38.0° and 40.0°-41.5° respectively.

TABLE II.  
Effect of Method of Addition of Reactants in Preparation of Xylylstearic Acid

Method	% of Distilland		
	Forerun b <sub>0.4</sub> 125-225° N.E. ap- prox. 300	Xylyl- stearic Acid b <sub>0.4</sub> 225-60°	Still Residue
Aluminum chloride added to oleic acid and xylene, Expt. 10.....	8	73	19
Oleic acid added to aluminum chloride and xylene, Expt. 11.....	27	64	9

TABLE III  
Synthesis of Compounds Related to Arylstearic Acids

Compound	Yield %	Boiling Point, °C.	n <sub>D</sub> <sup>25</sup>	d <sub>4</sub> <sup>25</sup>	Molecular Refractivity		% C.		% H.	
					Found	Theoretical	Found	Theoretical	Found	Theoretical
Xylyloctadecanol <sup>a</sup> (1.03 moles aluminum chloride added to 0.78 mole of oleyl alcohol and 5.7 moles of xylene; max. temp., 53°)	78	201-20 at 0.3 mm.	1.4925	0.8985	121.1	120.2	83.25	83.35	12.28	12.38
Phenyloctadecyl Phenylstearate <sup>b</sup> (0.1 mole each of the alcohol and acid; refluxed in xylene solution in presence of dry hydrogen chloride for 14 hours)	51	274-80 at 0.3 mm.	1.4935	0.9146	219.0	218.3	83.66	83.65	11.84	11.70
Methyl Phenylenedistearate <sup>c</sup> (1.65 moles aluminum chloride added to 0.5 mole of phenylstearic acid and 1.0 mole of oleic acid in petroleum ether. Product subsequently esterified with methanol in presence of dry hydrogen chloride)	29	238-73 at .04 mm.	1.4874	0.9283	207.2	204.9	78.67	78.75	11.82	11.72

<sup>a</sup> % OH, found, 4.65; theoretical, 4.54; color, Lovibond, 1" cell = 0.5Y.

<sup>b</sup> Sapon. equiv., found, 685.0; theoretical, 688.7.

<sup>c</sup> Sapon. equiv., found, 339.8; theoretical, 335.5.

### Summary

Twenty-six aromatic compounds were compared in the synthesis of arylstearic acids from oleic acid by the Friedel and Crafts reaction. Xylylstearic acid was the arylstearic acid obtained in the highest yield (92.4%) from technical m-xylene and commercial oleic acid. The various side reactions are discussed including the possible conversion of oleic acid into products which on vacuum distillation of the crude arylstearic acid appear as a forerun and as a still residue. Oleic acid of about 98% purity did not improve the yield but resulted in nearly colorless, rather than yellow viscous oils.

Crystalline arylstearic acids have for first time been isolated from the reaction products but only in small yields.

### Acknowledgment

The assistance of Edward T. Roe in the preparation of quantities of phenylstearic and xylylstearic acids is acknowledged.

TABLE IV  
Crystalline Arylstearic Acids

Aromatic Compound	Source of Oleic Acid	Yields, % of Theory		Melting Point °C.
		Crystal	Oil	
p-Xylene.....	Hydrogenated tallow	5.4	67.5	77.2-78.2
p-Xylene.....	"Solid" isoleic	0.2	22.0	76.0-77.6
p-Xylene.....	Red oil	0.7	78.3	76.8-77.8
p-Xylene.....	Olive oil	6.8	73.6	76.4-77.6
o-Xylene.....	Olive oil	2.5	74.7	59.8-61.2
p-Chlorotoluene.....	Olive oil	3.7	36.9	69.4-70.2
o-Chlorotoluene.....	Red oil	0.7	67.7	53.1-54.1
Benzene.....	Olive oil	0.4	60.3	64.8-65.4
		1.1	60.3	44.2-45.3

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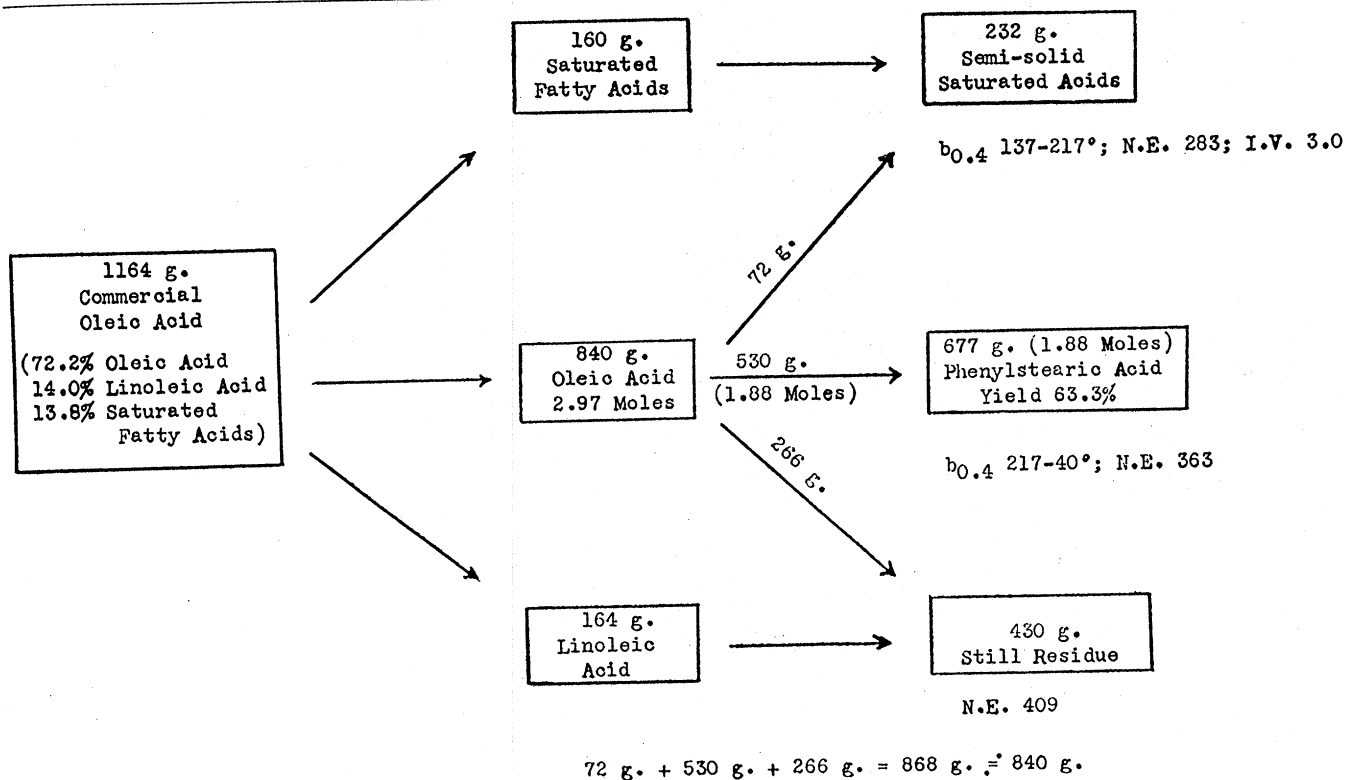


Fig. 1. Reactions in the preparation of phenylstearic acid.

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